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Thermally-induced loss of piezoelectricity in ferroelectric $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--BaTiO}_3$

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ABSTRACT

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1. Introduction

Piezoelectrics are used in various applications with a wide range of operating temperatures. Lead zirconate titanate (PZT) can exhibit a near-temperature-independent piezoelectric coefficient due, in part, to a vertical morphotropic phase boundary (MPB) [1]. By strict definition, MPBs are dependent only on composition and are independent of temperature, meaning that compositions near these boundaries should experience little change in the piezoelectric response over a wide temperature range. Compositions including Bi, such as $\text{BiScO}_3\text{--PbTiO}_3$, have also been considered for high temperature environments due to the presence of a near-vertical MPB and resulting high thermal stability of the piezoelectric properties [2,3]. However compositions containing Pb are subject to increased restrictions for use in consumer products. One key challenge in the development of Pb-free piezoelectric compositions is the retention of properties with increased temperature [4]. Thermal instability in most Pb-free piezoelectric materials is due to the lack of vertical MPBs similar to those found in PZT and

$\text{BiScO}_3\text{--PbTiO}_3$. Thermal stability can be limited because other phase transitions such as ferroelectric-to-ferroelectric are often found at temperatures much lower than the Curie point.

Sodium bismuth titanate (NBT; $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$) and NBT in solid solution with BaTiO_3 (BT) are compositions of interest in the development of Pb-free piezoelectric materials. The phase diagram of NBT–BT was originally reported by Takenaka et al. [5] and then later modified using Raman spectroscopy and electron microscopy [6–8]. In recent years, evidence of a lower symmetry structure has emerged from X-ray diffraction [9–11], electron microscopy [12], and pair distribution function [13] measurements, leading to updated phase diagrams [14]. The phase assignment is also subject to the electrical poling history [15]. Given the structural complexities of NBT–BT, it is challenging to predict the impact of the phase transition sequence on the temperature-dependent loss of piezoelectricity, or thermal depoling. An experimental investigation of this thermal stability is therefore important.

The objective of the present work is to explore the thermal stability of electrically poled $(1-x)\text{NBT}-x\text{BT}$ (NBT– $x\text{BT}$) polycrystalline piezoelectric materials as a function of composition (x) and correlate this behavior with the known equilibrium phases and phase transitions. Samples with compositions $x \leq 13\%$ are investigated using Raman spectroscopy and thermal depoling, the latter involving the change in piezoelectric coefficient with

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exposure to increased temperatures. Raman spectroscopy is used to help interpret the structural origin of depoling due to its sensitivity to phase changes and short-range disorder.

2. Experimental procedure

Solid solutions of NBT–*x*BT with concentrations of BT ($x=0, 4, 6, 9$, and 13%) were processed via solid state reaction. These BT concentrations were selected in order to examine the distinct equilibrium regions of the phase diagram [5,8,15]. As an MPB is known to exist at approximately $x \approx 6\text{--}7\%$, compositions were selected both near and on either side of the MPB. The A-site cations (Ba^{2+} , Na^+ , and Bi^{3+}) were adjusted by assuming that Ba equally occupies the Bi and Na sites. Reactant powders (Alfa Aesar) of Bi_2O_3 (99.975%), TiO_2 (99.6%), Na_2CO_3 (99.5%), and BaTiO_3 (99.7%) were ball milled for 24 h and then calcined in the range $900\text{--}950^\circ\text{C}$. The calcined powder was uniaxially pressed at 200 MPa for 5 min followed by isostatic pressing at 250 MPa for 5 min. The pellets were sintered between $1100\text{--}1150^\circ\text{C}$, with the selected temperature increasing proportional to the amount of barium.

Electrical poling was conducted in an oil bath for 5 min at room temperature. The field amplitude used for poling varied with BT concentration and was lower than the breakdown voltage of each composition. Poling fields for $x=4, 6, 9$, and 13% were 4, 2, 3, and 3 kV/mm, respectively. After 24 h, the direct longitudinal piezoelectric coefficient (d_{33}) was measured using a Berlincourt meter (APC Ceramics, Mackeyville, PA).

Depoling experiments were conducted using a heated oil bath at fixed temperatures. The oil temperature was measured using both a thermocouple and a mercury thermometer. Continuous stirring of the oil bath was required to maintain a uniform temperature. The temperature was raised in increments of 10°C starting from room temperature. At each temperature, all the samples of various compositions were immersed in the heated oil at the same time for 5 min. The temperature was recorded immediately prior to and after sample immersion. After each sample immersion, the d_{33} was recorded. The reported value is the average of the measurements recorded five times in both the positive and negative direction.

Raman spectra were obtained on unpoled samples of all compositions with a LabRAM microprobe system (ISA/Jobin-Yvon/Horiba, Villeneuve d'Ascq, France) using a 532.02 nm Nd:YAG solid state laser as the excitation source. The laser light was focused on the (mirror-polished) sample surface by means of a long working distance $100\times$ (N.A.=0.8) objective lens (LMPlan FI, Olympus, Tokyo, Japan), allowing the spot width to be $\sim 1\text{ }\mu\text{m}$ on the illuminated location. Effective power at the sample surface was set to 3 mW. Spectra were collected in a true backscattering geometry with the aid of a Peltier-cooled Charged Coupled Device camera. Temperature-dependent (*in situ*) Raman experiments were performed using a Linkam MDS600 heating-cooling stage (Linkam, Tadworth, UK). Temperature stability of the stage was checked by monitoring the phase transition points of CO_2 and H_2O inclusions in transparent minerals. The collected spectra were deconvoluted and analyzed in a commercial software environment (Labspec 4.02, Jobin-Yvon/Horiba) using Gaussian–Lorentzian peak functions.

3. Results and discussion

The d_{33} values are reported as a function of composition (Fig. 1 and Table 1) and temperature (Fig. 1). Initial d_{33} values are generally consistent with the trends in Jo et al. [15]; the d_{33} of

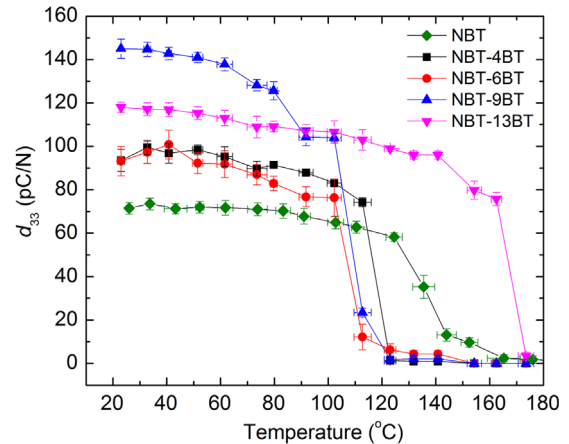


Fig. 1. d_{33} of NBT–*x*BT piezoelectric materials as a function of depoling temperature.

Table 1

Initial d_{33} values and T_d obtained from depoling and Raman experiments.

Composition	d_{33} [pC/N]	T_d (depoling) [$^\circ\text{C}$]	T_d (Raman) [$^\circ\text{C}$]
NBT	71.5	135	–
NBT+4% BT	93.5	116	125
NBT+6% BT	93.2	107	105
NBT+9% BT	145	106	–
NBT+13% BT	118	165	–

NBT is increased by substitution of Ba (increasing x) and the tetragonal side of the MPB (e.g., $x=9\%$ and 13%) exhibits higher values than the rhombohedral side (e.g., $x=4\%$). Near the MPB ($x=6\%$), the value measured is slightly lower (approximately 93 pC/N) than the values measured on the tetragonal side (> 100 pC/N). Recently, it has been observed that the d_{33} of MPB compositions such as $x=6\%$ can be strongly dependent upon the maximum field amplitude during poling [16], which is attributed to the onset of complex phase mixtures and microstructures. Such an effect may explain the result in the present work that the MPB composition exhibits a lower d_{33} value than compositions on the tetragonal side of the MPB.

Two different qualitative behaviors of thermal depoling were observed in the NBT–*x*BT compositions: an abrupt decrease in d_{33} with temperature was observed in compositions with $x \geq 4\%$, whereas a smoother decrease in d_{33} occurred in the unmodified NBT. Similar trends were observed in Fe^{3+} -modified NBT [17], i.e. the smooth thermal depoling behavior is changed to a more abrupt one. However, it was also observed that La^{3+} modification resulted in smooth depoling behaviors similar to that of NBT [18]. Anton et al. [19] also observed smoother depoling behaviors in PZT than in BaTiO_3 . The origin of this qualitative difference is not known in the present work, but may be associated with different types of phase transitions in different compositions and systems.

The decrease in d_{33} with temperature can be characterized by a singular depoling temperature (T_d) value, defined in Davies et al. as the temperature at which the piezoelectric coefficient is reduced to half of its original value [20]. The values of T_d extracted from Fig. 1 are tabulated in Table 1. The composition $x=13\%$ exhibits the highest T_d (165°C), while compositions of $x=6\%$ and 9% exhibit the lowest T_d values. The observation of the lowest T_d in compositions of $x=6\%$ and 9% is consistent with the supposition that the MPB is near or between these compositions and experimental evidence that suggests its presence in this compositional range [16].

Room-temperature Raman spectra for the investigated compositions are shown in Fig. 2(a). A notable feature is the splitting of the A_1 mode at $\sim 270\text{ cm}^{-1}$ in BT concentrations of $x \geq 4\%$, and the splitting amplitude increases with increasing x . Across this phase boundary, the structures change from a monoclinic Cc space group at low x [14,21] to tetragonal or mixed phases at higher x . This would involve a decrease in the number of Raman-active modes as calculated from group theory. The number of Raman-active modes in monoclinic Cc is 27 ($\Gamma_{\text{Raman},Cc} = 13A' + 14A''$), whereas for the tetragonal $P4bm$ space group only 16 Raman modes should be active ($\Gamma_{\text{Raman},P4bm} = 4A_1 + B_1 + 3B_2 + 8E$) [22]. Since an apparent increase of Raman modes in the spectral signature was observed, group theory cannot be used to interpret this result. This is somewhat common in systems where translational and substitutional disorder is present [23]. The increase in the number of modes with x may not be due to new modes appearing, but rather to a shift of the main components of the feature at $\sim 270\text{ cm}^{-1}$, likely related to increased strain between A-site and oxygen atoms upon Ba substitution. This shift has been observed in similar

systems with A-site substitution, and may be linked to the onset of a mixed and/or relaxor phase [24]. Another notable feature is that the spectral signature broadens with x . This is related to the increment of translational disorder upon substitution of Bi with Ba or Na at the perovskite A-site, which is expected to impact the vibrational modes associated with the oxygen octahedron (above 200 cm^{-1}) [25].

Increasing temperature to above T_d , the Raman spectra of all compositions broaden and resemble spectra typical of a pseudocubic (long-range cubic, short-range distorted) structure above 200°C (cf. Fig. 2(b) and (c) show two example compositions). The splitting of the A_1 mode at $\sim 270\text{ cm}^{-1}$ appears to cease at a temperature in the region of the T_d . This effect however, may not be related to a structural change occurring at T_d , but may simply be ascribed to anharmonic effects related to increasing temperature (i.e. broadening of the spectral signature). To detect changes in the short-range atomic arrangement, the A_1 mode position at 270 cm^{-1} is shown with increasing temperature in Fig. 3. As this mode is related to Ti–O vibrations, an anomaly in the softening

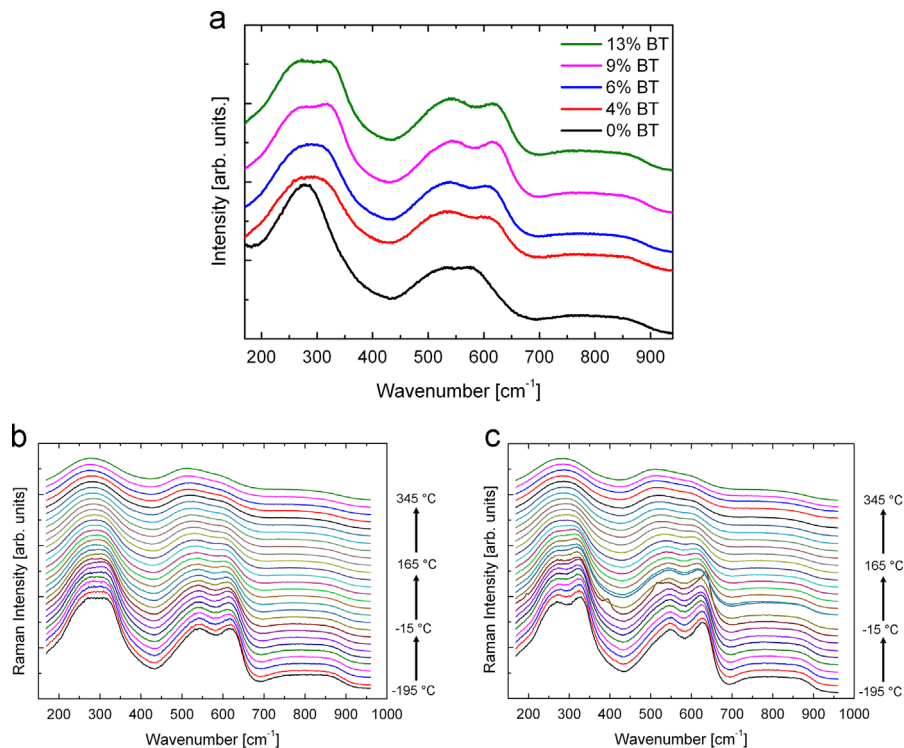


Fig. 2. (a) Room-temperature Raman spectra of NBT–xBT piezoelectric materials; Temperature-dependent Raman spectra for two representative compositions (b) $x=6\%$, and (c) $x=9\%$.

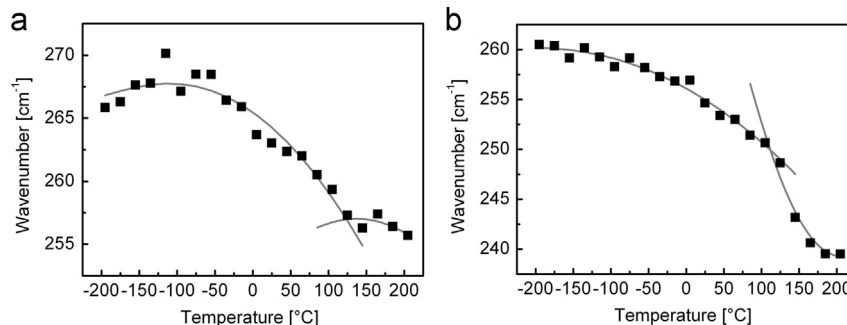


Fig. 3. Mode position versus temperature for two representative compositions: compositions: (a) 4% BT, and (b) 6% BT.

with temperature generally indicates a short-range structural rearrangement associated with a second-order phase transition. The Balkanski formula may be used to reproduce anharmonic phonon softening [26–28]:

$$\omega(T) = \omega_0 + A \left[1 + \frac{2}{e^x - 1} \right] + B \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (1)$$

where $x = \hbar\omega_0/2kT$, $y = \hbar\omega_0/3kT$, with k the Boltzmann's constant and \hbar the reduced Planck's constant; A , B and ω_0 are fitting parameters, and T is temperature. In the absence of a phase transition with increasing temperature, phonon softening is defined by Eq. (1). In the case of anomalies in the phonon softening behavior, more than one of these curves may exist. The point where two such adjacent curves join can be regarded as the second order phase transition temperature [27,28]. The solid lines in Fig. 3 represent fitting of the experimental data performed using Eq. (1) to the two compositions that yielded the most reliable fits; the anomaly temperature can be identified for each of these compositions. These temperatures correlate well with the measured T_d by thermal depoling (cf. Table 1). The difficulty in detecting anomaly temperatures for compositions of $x \geq 9\%$ could be explained by the increase of local disorder induced by Ba substitution. Moreover, differences between the anomaly temperature and T_d might be ascribed to the fact that Raman was applied to unpoled samples whereas the thermal depoling measurements were undertaken on poled samples. The anomalies observed in the $x=4\%$ and $x=6\%$ compositions can be associated with local rearrangements of the Ti–O bond [28], possibly due to the change in the distribution of bonds parallel to $[001]_c$, e.g., the nucleation of $P4bm$ nanodomains.

4. Conclusions

The present work reports the thermal depoling and loss of piezoelectricity in compositions of NBT– x BT in the range $0 \leq x \leq 13\%$. The lowest depoling temperature was measured in compositions that are near the MPB ($x=6\%$). An abrupt decrease in piezoelectric coefficient was measured during depoling of compositions $x \geq 4\%$ whereas $x=0\%$ exhibited a less abrupt depoling behavior. The Raman spectra of concentrations $x \geq 4\%$ exhibited an apparent increase in the number of modes relative to unmodified NBT, which is interpreted as a change in symmetry towards space groups consistent with phase diagrams for NBT– x BT. The broad appearance of the Raman signature with increasing BT concentration hints to a more disordered structure than unmodified NBT.

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